

# Partial Replacement of Portland Cement with Fly Ashes and Kiln Dusts Using Supercritical Carbon Dioxide Processing

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## Abstract

The natural curing reactions which occur in a standard portland cement involve the formation of portlandite,  $\text{Ca(OH)}_2$ , and calcium silicate hydrates, CSH. Over time, a cured cement absorbs carbon dioxide ( $\text{CO}_2$ ) from the air, converting the portlandite and some of the CSH to calcium carbonate,  $\text{CaCO}_3$ . Although this carbonation reaction is thermodynamically-favorable, the conversion of  $\text{Ca(OH)}_2$  to  $\text{CaCO}_3$  results in the blockage and/or closure of pores, which impedes the ingress of reactants ( $\text{CO}_2$ ) and the egress of reaction products ( $\text{H}_2\text{O}$ ), drastically slowing the reaction rate with time. By exposing a portland cement to the reactant ( $\text{CO}_2$ ) in the supercritical state, the rate of the carbonation reaction can be greatly accelerated. This acceleration is due to (1) the ability of the supercritical fluid to penetrate into the pores of the cement, providing continuous availability of fresh reactant, in hyper-stoichiometric concentrations; and (2) the solubility of the reaction product in the supercritical fluid, facilitating its removal. By accelerating the natural carbonation reaction, a chemically stable product is formed having reduced porosity, permeability and pH, while at the same time significantly enhancing the mechanical strength.

The  $\text{CaCO}_3$ , formed in large amounts during the carbonation, has excellent cementing properties, allowing us to replace much of the portland cement with materials such as fly ash and kiln dusts, which have inferior cementing properties. Portland cement, modified with ashes and dusts, displays distinct advantages as low-cost building materials and as immobilization matrices for the solidification/stabilization of heavy metals and radionuclides.

## 1. Introduction

### 1.1. SUPERCRITICAL FLUIDS

The temperature at which the vapor pressure above a pure liquid reaches one atmosphere is known as the normal boiling point. For water, the normal boiling point at one atmosphere is  $100^\circ\text{C}$ . In an open container, Figure 1, the temperature of liquid water cannot be raised above  $100^\circ\text{C}$  since this would cause the vapor pressure of the water to rise above one atmosphere, which would exceed the ambient pressure conditions. If we place a quantity of water in a sealed container, however, then we may heat the liquid water to temperatures greater than  $100^\circ\text{C}$ , since the vapor pressure of the water can increase beyond one atmosphere. As we uniformly heat the sealed container, the density of the liquid water decreases through thermal expansion. Simultaneously, the density of the water vapor increases. We can continue this heating process until, eventually, the density of the liquid becomes so reduced, and the density of the vapor is so increased, that the two densities become equal. The temperature at which the liquid and vapor densities become equal is called the critical temperature. Since the temperature inside the sealed container is everywhere equal, and the density is everywhere equal, thermodynamics dictates that the pressure inside the container be everywhere equal. This pressure is called the critical pressure. A fluid which has been brought to conditions above its critical temperature and pressure is known as a supercritical fluid (SCF). This physical description of the formation of the supercritical fluid state suggests that all simple fluids can be made supercritical by generating the

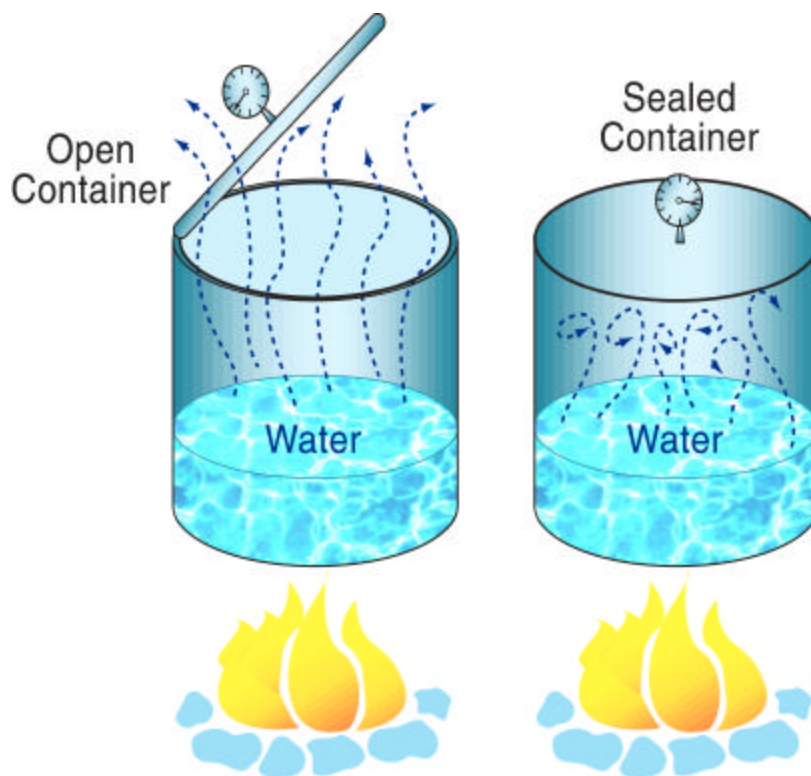


Figure 1. Formation of a supercritical fluid by heating a liquid in a sealed container.

appropriate conditions of temperature and pressure. This is indeed correct, and Table 1 gives the critical temperature and pressure of some common fluids.

SCF's are used as solvents in many commercial processes, including the extraction of caffeine from coffee and essential oils and spices from plants for use in perfumes and foods. The attractiveness of supercritical fluids as solvents stems from their unique combination of liquid-like and gas-like properties. A comparison is given in Table 2 of the diffusivity, viscosity and density of a typical organic fluid in the liquid, gas, and supercritical fluid states. To a first approximation, the solvent power of a fluid is related to its density. The high, liquid-like densities achievable in supercritical fluids

Table 1. Critical Temperature and Pressure for some Common Fluids.

Fluid	Critical temperature (°C)	Critical Pressure (psi)
Neon, Ne	-229	400
Nitrogen, N <sub>2</sub>	-147	492
Argon, Ar	-122	706
Xenon, Xe	17	858
Carbon dioxide, CO <sub>2</sub>	31	1072
Sulfur hexafluoride, SF <sub>6</sub>	46	545
propane, C <sub>3</sub> H <sub>8</sub>	97	617
ammonia, NH <sub>3</sub>	133	1654
water, H <sub>2</sub> O	374	3209

Table 2. Comparison of physico-chemical properties of a typical organic fluid in the liquid, gas, and supercritical fluid state.

	Diffusivity (cm <sup>2</sup> /s)	Viscosity (cP) or (mN·s/m <sup>2</sup> )	Density (kg/m <sup>3</sup> )
Liquid	10 <sup>-5</sup>	1	1000
Supercritical Fluid	10 <sup>-3</sup>	10 <sup>-2</sup>	300
Gas	10 <sup>-1</sup>	10 <sup>-2</sup>	1

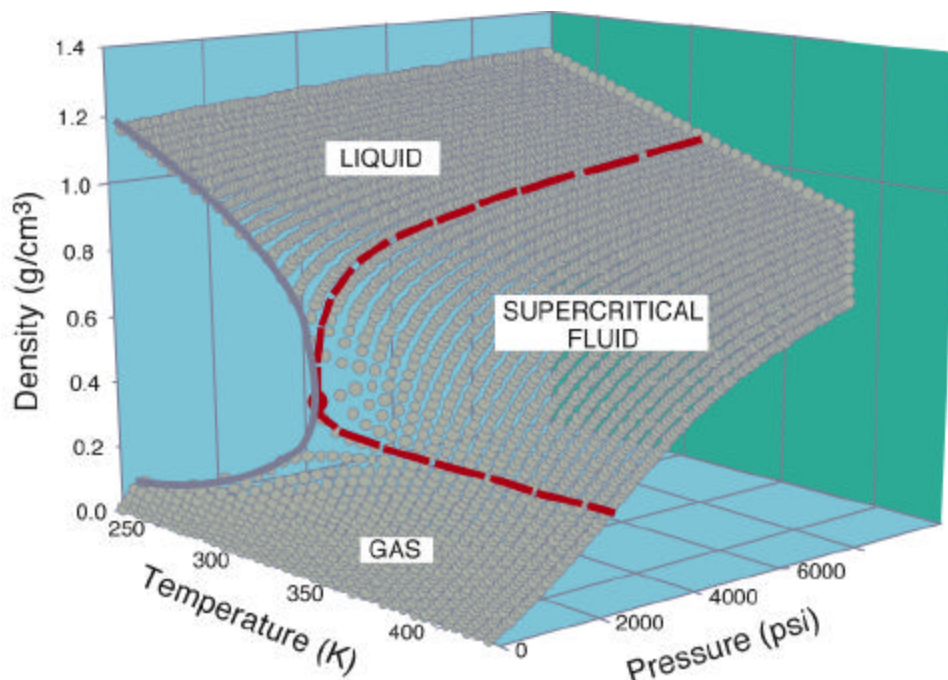


Figure 2. Pressure-temperature-density surface of pure CO<sub>2</sub>.

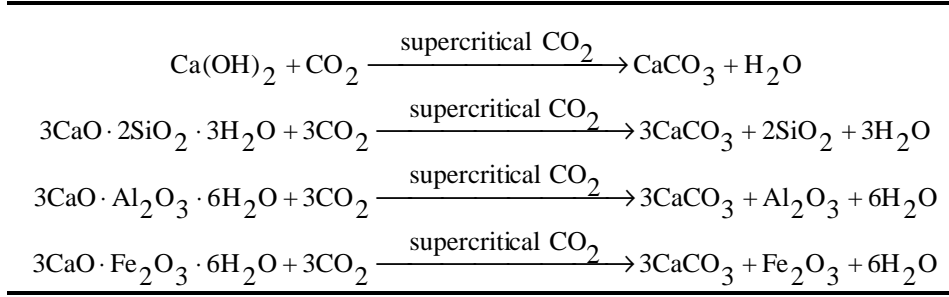
therefore allows for substantial solubilities. Figure 2 shows the pressure-temperature-density surface for pure CO<sub>2</sub>. The critical point for pure CO<sub>2</sub>, 31°C or 88°F and 1072 psi or about 73 atmospheres, is shown in Figure 2 by the dark, solid circle. It can be seen that relatively small changes in temperature or pressure, near the critical point, result in large changes in density. It is this tunability of density, and therefore tunability of solvent power, which is the most attractive attribute of supercritical fluids. Also, the gas-like properties of low viscosity and high diffusivity of supercritical fluids, Table 2, provides for effective mass transport into granular and micro-porous matrices, such as cements. Finally, the absence of surface tension provides for excellent wettability.

Supercritical CO<sub>2</sub> is an excellent choice for large-scale extraction and treatment processes for several reasons. CO<sub>2</sub> is non-toxic, non-flammable, and inexpensive (10 - 40 cents per pound of liquid). Its critical conditions of temperature and pressure are easily achievable in existing process equipment. Also, there exists a well-developed transportation infrastructure (most all restaurants serve carbonated drinks, which require the use of compressed CO<sub>2</sub> cylinders). We have been applying this unique combination of chemical, physical and economic properties of supercritical fluid CO<sub>2</sub> to enhance the performance of unmodified portland cements and portland cements modified by the addition of low-grade pozzolans, such as fly-ash and kiln dusts.

## 1.2. APPLICATION TO UNMODIFIED PORTLAND CEMENT

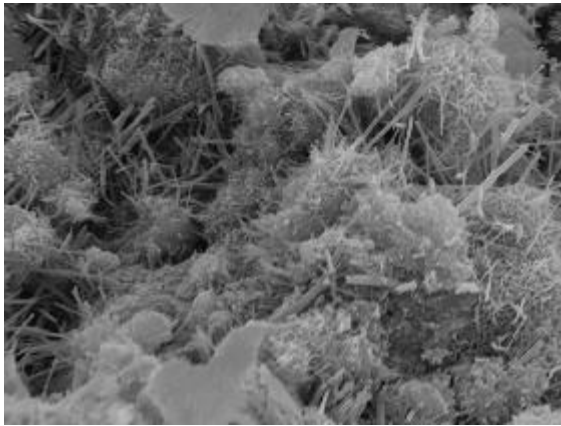
The natural curing reactions which occur in a standard portland cement involve the formation of calcium hydroxide (portlandite), Ca(OH)<sub>2</sub>, as well as hydrated calcium silicates (CSH). Over time, the cement will absorb CO<sub>2</sub> from the air, converting the Ca(OH)<sub>2</sub>, and some of the CSH, to CaCO<sub>3</sub> through reactions such as those shown in Table 3. It turns out, however, that the molar volume of CaCO<sub>3</sub> is larger than that of Ca(OH)<sub>2</sub>, resulting in the closure and/or blockage of pores, impeding the ingress of reactant, CO<sub>2</sub>, and the egress of reaction product, H<sub>2</sub>O. An example of the chemical and structural changes produced by supercritical CO<sub>2</sub> treatment of unmodified portland cement/sand mortar are shown in Figures 3 and 4. The net result is that the carbonation reaction begins rapidly, but then drastically slows with time. The oldest, man-made cement structures, such as those in Greece and China, are still undergoing this carbonation reaction, even after several thousand years...

*Table 3. Idealized reactions for the supercritical CO<sub>2</sub> carbonation of unmodified portland cement.*

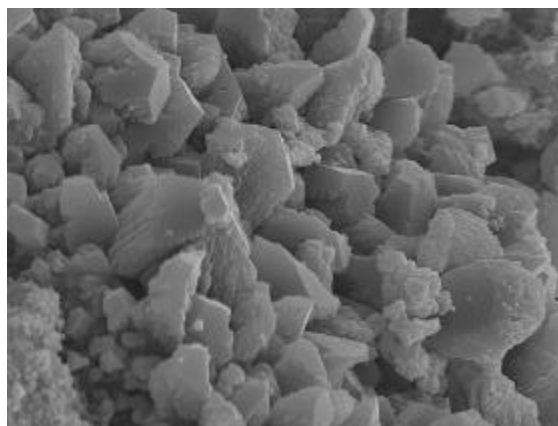


By exposing a portland cement to supercritical CO<sub>2</sub>, it is found that the carbonation reaction can be greatly accelerated. This acceleration is due to the ease of penetration of the supercritical fluid into the micro-pores of the cement, providing continuous availability of hyper-stoichiometric, fresh reactant, as well as the ability of the dense CO<sub>2</sub> to solubilize the reaction product, facilitating its removal. Figure 5 shows x-ray diffraction (XRD) pattern for a 6" × 12" cement cylinder which was treated with supercritical CO<sub>2</sub> for a length of time sufficient only to produce a reaction in the outer portion of the cylinder. It can be seen that the pattern for the outer portion of the cylinder indicates a nearly complete conversion of Ca(OH)<sub>2</sub> to CaCO<sub>3</sub>, while the pattern for the inner portion shows minimal conversion. We observe generally that the supercritical CO<sub>2</sub> treatment results in a carbonation, whose depth depends on the initial porosity, permeability, and free-water content of the cement. By suitable adjustment of these parameters, we have demonstrated complete carbonation in cement samples during a treatment time of several hours.

In order to efficiently carbonate large pieces of portland cements, we need to supply the CO<sub>2</sub> in large stoichiometric excess so as to dissolve the reaction product, H<sub>2</sub>O. Further, the CO<sub>2</sub> must be supplied at a flow rate sufficiently high so that the water content in the CO<sub>2</sub> does not build-up, which would inhibit the reaction. This is best achieved using a closed-loop, recirculating system, where the CO<sub>2</sub> is continuously scrubbed of the dissolved reaction product. Figure 6 shows a schematic pressure-temperature phase diagram for CO<sub>2</sub>, which also incorporates a process flow diagram for a closed-loop cement treatment system. The treatment cycle begins with a liquid-CO<sub>2</sub> storage reservoir. The liquid is brought to above its critical pressure during a pumping operation, which sends the pressurized liquid to a heating unit. The heating unit warms the pressurized CO<sub>2</sub> to above its critical temperature, forming a SCF. The SCF enters the treatment vessel and is brought into contact with the cement. During this time



*Figure 3. Micrograph of unmodified portland cement/sand mortar before supercritical CO<sub>2</sub> carbonation.*



*Figure 4. Micrograph of unmodified portland cement/sand mortar after supercritical CO<sub>2</sub> carbonation.*

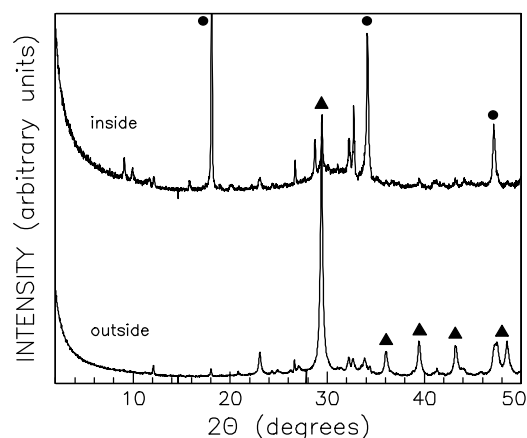


Figure 5. X-ray diffraction spectra of the inside and outside portion of a 6" x 12" portland cement cylinder partially reacted with supercritical CO<sub>2</sub>. The circles identify the peaks due to Ca(OH)<sub>2</sub>, while the triangles show the diffraction peaks due to CaCO<sub>3</sub>.

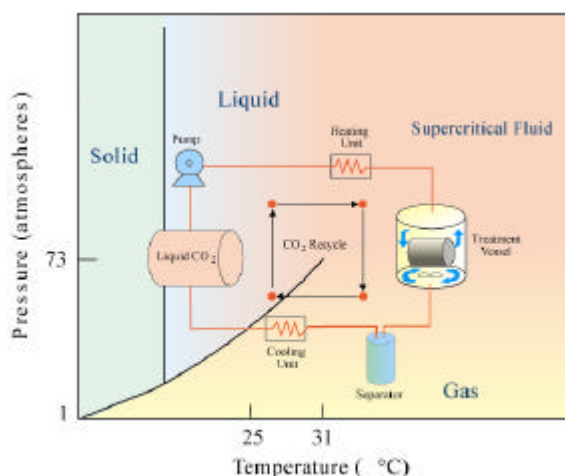


Figure 6. Pressure-temperature phase diagram of pure CO<sub>2</sub> with a superimposed flow diagram for a closed-loop supercritical fluid treatment process.

the water is extracted from the cement and solubilized in the CO<sub>2</sub>. There is a constant flow of CO<sub>2</sub> through the treatment vessel, so that clean, dry CO<sub>2</sub> is continuously made available. In the supercritical state, the density of CO<sub>2</sub> is sufficient to dissolve up to several mole percent of water, so that a flowing system can remove large amounts of water in relatively short times. On exiting the treatment vessel, the supercritical CO<sub>2</sub>, containing the dissolved water, is sent to a separation vessel, where the fluid is de-pressurized. As the pressure decreases to below the critical pressure, the CO<sub>2</sub> expands into a gas, with a large decrease in density. Since the solubility of the entrained water is proportional to the CO<sub>2</sub> density, the water falls out of solution and is deposited in the bottom of the separator. The clean, dry CO<sub>2</sub> gas exits the top of the separator, where it is condensed to a liquid by a cooling unit before re-entering the storage vessel. This type of closed-loop extraction means that there are no uncontrolled waste streams exiting the extraction system. All of the extracted materials are retained in the separation vessel for subsequent analysis, treatment, recycle and/or disposal. Further, the extracted materials are concentrated in the separator, reducing the volume of waste.

The SuperScrub™, which is part of the Supercritical Fluids Facility at the Los Alamos National Laboratory, is a just such a fully-automated, closed-loop supercritical CO<sub>2</sub> treatment system. The liquid CO<sub>2</sub> storage vessel has a capacity of 100-liters, and the treatment vessel has a 60-liter capacity. The treatment vessel operates at pressures up to 5000 psi, temperatures up to 80°C, and flow rates up to 500 pounds/hr. There is a 500 rpm magnetic impeller inside the extraction vessel, which aids in the carbonation process by agitating the supercritical fluid.

We have conducted treatment experiments on cylindrical cement samples up to 6" diameter x 12" length, where we achieve nearly complete carbonation (water removal) in a treatment time of several hours. We find generally that the supercritical CO<sub>2</sub> treatment of portland cements results in an increased density and increased strength. Further, the strength enhancement improves with the total curing time, indicating that the maximum strength enhancements will be achieved for cements which have been allowed to fully cure for a period of several weeks. However, the curing process itself can be accelerated by steam curing. This can easily be accomplished in the same pressure vessel used for the SCF treatment.

### 1.3. APPLICATION TO FLY ASH MODIFIED PORTLAND CEMENT

We have been investigating two broad areas of application for portland cement incorporating industrial waste, and its treatment using supercritical CO<sub>2</sub>. The first is the utilization of solid wastes,

generated as by-products of industrial processes, as additives to conventional cements to be used as low-cost building materials. One such waste material is fly ash from coal fired power plants. Because the  $\text{CaCO}_3$  formed during the carbonation reaction is itself chemically stable and an excellent cementing agent, it is possible to replace a large fraction of the portland cement with fly ash, while maintaining similar levels of durability and mechanical strength. Our conception of a supercritical  $\text{CO}_2$ /fly ash plant integrated with a coal-fired power plant is shown in Figure 7. The fly ash would be filtered from the effluent gas stream, while the  $\text{CO}_2$  would be separated from the stack gases, downstream from the particulate filter. The fly ash is blended with a minor fraction of cement powder, water, and additional chemicals as necessary, to produce a paste, moldable into a desired product. Once formed into a final shape, the molded product is cured for a time, and then treated with supercritical  $\text{CO}_2$ , derived from the recovered stack-gases and waste heat scavenged from heat exchangers. This fabrication process allows us to utilize the three main waste products of coal-derived power generation : fly ash,  $\text{CO}_2$ , and heat, combining them into a salable product to recover overall operating costs (and eliminating disposal costs for the fly ash, amounting to roughly 14 dollars per ton). As an example of the products that can be made with supercritical  $\text{CO}_2$ -processed, fly-ash modified cements, Figure 8 shows roofing tiles, produced by extrusion of a 80 vol.% fly ash, 20 vol.% portland cement slurry and subsequently treated with supercritical  $\text{CO}_2$ .

The second general area of application is the enhancement of cement which is itself an industrial waste. By this we mean cements used to immobilize environmentally-regulated metals and radioactive elements. For example, in order to meet present Department of Energy (DOE) transportation and storage requirements, cemented wasteforms must satisfy several requirements,[1] including a maximum limit on the radioactive decay heat. Decay heat is defined as the heat produced by radioactive emissions that are absorbed in the surrounding materials. The current decay heat limit is based, in part, on the overall hydrogenous content of the cement. If the hydrogenous content of the cement (primarily water) can be reduced to less than 30 percent by weight, then the maximum allowable decay heat for this modified cement increases fourfold.[2] This treated cement would not only ensure compliance with transportation and storage regulations, but would reduce the overall

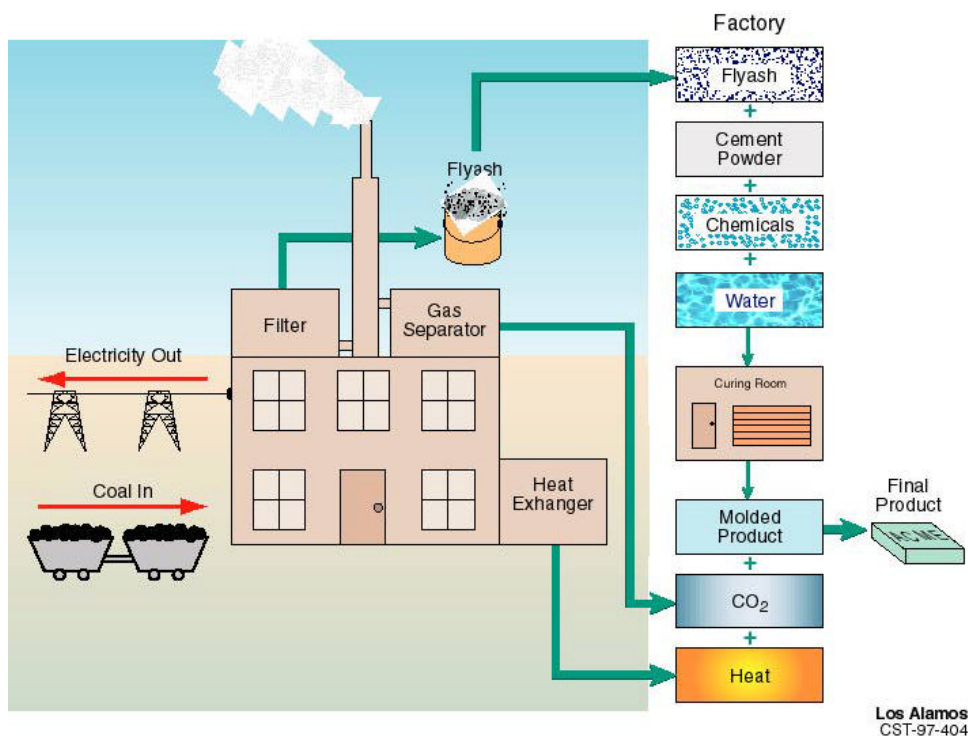
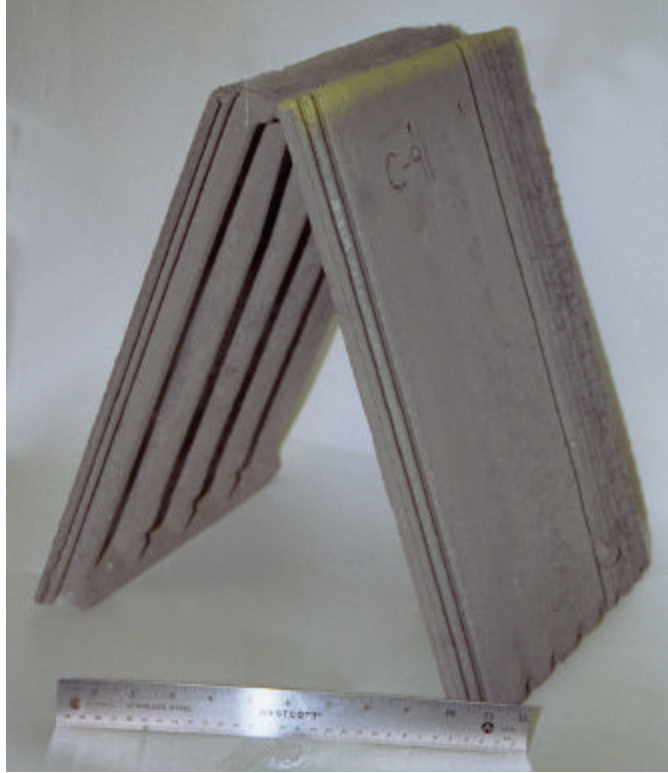


Figure 7. Schematic illustration of a supercritical  $\text{CO}_2$ /fly ash plant integrated with a coal-fired power plant.





*Figure 8. Roofing tiles, extruded from a 80 vol.% fly ash, 20 vol.% portland cement slurry and treated with supercritical CO<sub>2</sub>.*

volume of cemented waste requiring disposal.

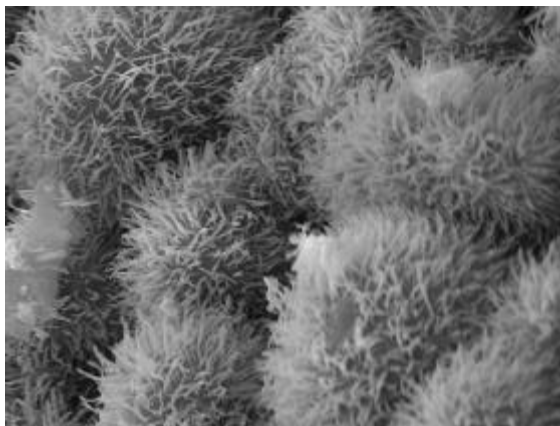
The incorporation of fly ash into portland cement has been identified as one of the treatment parameters of cement composition to be evaluated. There is already an extensive “experience database” on the performance of fly ash-modified portland cement for heavy metal immobilization and the solidification/stabilization (S/S) of radioactive waste. The United Kingdom [3] and the United States [4] have used these materials, in the form of cement grouts, for the S/S of low- and intermediate-level radioactive wastes. In this section, we will review the known benefits of fly ash-modified portland cement over unmodified portland cement, along with the anticipated improvements expected by the supercritical CO<sub>2</sub> treatment of modified portland.

- Fly ash increases the density, decreases the permeability, and increases the leaching resistance of OPC. It is a truism that “The leach resistance of solidified cement-waste systems can be improved by any process which accelerates curing, limits porosity, or chemically bonds fission product or actinide elements.”[5]. SCCO<sub>2</sub> treatment of a modified portland cement is expected to further increase the density over the untreated material, so that a reduced porosity, and improved leachability should result. In addition, the high silica content of fly ash, with its well-known sorbent properties towards actinides and certain other radionuclides, enhances the immobilization characteristics, Table 4.
- The presence of heavy metals is often observed to significantly interfere with proper setting of portland cement. The incorporation of fly ash into portland cement helps to partially compensate for this set-retardation, and a subsequent supercritical CO<sub>2</sub> treatment of such a modified cement should perform even better.

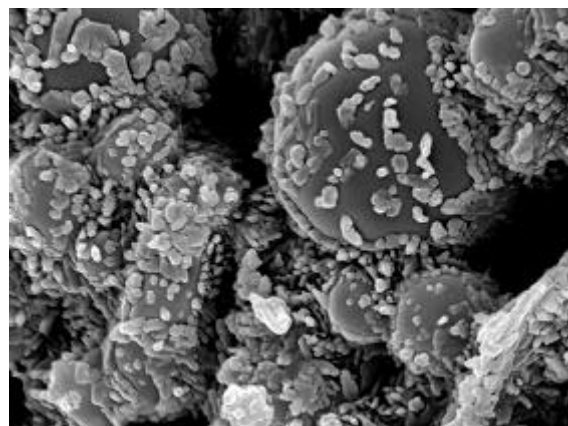
*Table 4. Modified portland cement compositions for the immobilization of heavy metals.[6]*

<b>Metal</b>	<b>Good</b>	<b>Better</b>	<b>Best</b>
Lead	Type I cement	Type I cement with silica fume	Type V with silica fume and a little extra gypsum
Cadmium	Cement with silica fume	Higher cement factor, no silica fume	Still more cement for long-term durability
chromium	Portland cement	Portland cement with silica fume	Same but with oxidation inhibitor to avoid hexavalent chromium
Arsenic	Portland cement with added $\text{FeSO}_4$	Portland cement with pre-oxidation with $\text{H}_2\text{O}_2$ and added $\text{FeSO}_4$	Same, but with higher cement factor and higher Fe/As ratio
mercury	Portland cement	Higher cement factor	Even more cement to ensure strongly reduced porosity

- Fly ash incorporation improves the fluidity of a portland cement mix, which improves workability. For solidification/stabilization applications, this increased fluidity may allow a reduced water/cement ratio to be used in the casting operation.
- The incorporation of fly ash lowers the initial heat evolution during setting, reducing the incidence of cracking and spalling. It is desirable to maintain the modified cement in monolithic form for optimum leach resistance.
- Fly ash, as it is typically generated in a high free-carbon environment, contains iron in a reduced state, which helps to lower the redox potential in the cement. Maintaining both heavy metals, such as Cr, and radionuclides in lower oxidation states should result in lower solubilities, and reduced leachabilities.
- Since the  $\text{SCCO}_2$  treatment converts the alkaline phases into neutral pH phases, a straight or fly ash-modified portland cement which has been carbonated will have a much reduced pH. In portland cement, the highly alkaline environment precipitates actinide elements as hydroxides, rendering them immobile. We have recently begun experiments to evaluate the effect of supercritical  $\text{CO}_2$  treatment, and the attendant pH reduction, on the leachability of actinide surrogates. We have shown that the treatment decreases the leachability, by incorporating the surrogate elements within carbonate phases and in de-calcified regions adjacent to these carbonate phases.
- While portland cement is considered to be an inexpensive immobilization matrix, relative to other candidate materials, its cost is expected to rise in light of current and future projected shortages. Fly ash, as it is a large-volume industrial waste, is both cheap and abundant, so that there is an



*Figure 9. Micrograph of cemented fly ash microspheres before supercritical  $\text{CO}_2$  treatment.*



*Figure 10. Micrograph of cemented fly ash microspheres after supercritical  $\text{CO}_2$  treatment.*



economic incentive to use fly ash-modified cements. In addition, CO<sub>2</sub> is also produced as a waste by-product of industrial processes (power generation, cement manufacture, *etc.*), and its permanent sequestration into cement is an added environmental benefit. A fully-carbonated portland cement permanently sequesters about 130 liters of CO<sub>2</sub> per kilogram of cement.

Figures 9 and 10 show the structural and chemical modifications produced in cemented fly ash microspheres as a result of the supercritical CO<sub>2</sub> treatment. As is the case with fly ash, kiln dusts are primarily siliceous, so that the same benefits can be derived from their use as modifiers in immobilization and S/S matrices.

### III. Conclusions

We have demonstrated that supercritical CO<sub>2</sub> can be used to accelerate the natural carbonation reactions in unmodified portland cements, and that this treatment enhances the physical properties of the cement. Further, it has been proven that the use of supercritical CO<sub>2</sub> allows the replacement of portland cement powder with inexpensive, lower-grade pozzolans, such as fly ashes. By integrating a supercritical CO<sub>2</sub> facility with a pozzolan manufacturer, such as a cement plant, we can, in effect, close the CO<sub>2</sub> loop on the cement-manufacturing process, Figure 11.

### III. Acknowledgements

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### IV. References

1. U.S. DOE (1992) "TRUPAC-II User Requirements Document", Rev. February 2.
2. U.S. DOE (1996) "TRUPAC-II Content Codes (TRUCON)", Rev. 10, DOE/WIPP 89-004.
3. Wilding C.R. "The Performance of Cement Based Systems", Cement and Concrete Research 22 (1992) p. 299.
4. Huang, F.H., D.E. Mitchell, and J.M. Conner, "Low-Level Radioactive Hanford Wastes Immobilized by Cement-Based Grouts", *Nuclear Technology*, 107 (1994) p. 254.
5. Jantzen C.M., F.P. Glasser, and E.E. Lachowski, "Radioactive Waste-Portland Cement Systems: I, Radionuclide Distribution", *J. Am. Chem. Soc.*, 67 (1984) p. 668.
6. C.M. Wilk "Stabilization of Heavy Metals with Portland Cement : Research Synopsis", Portland Cement Association Report IS007 (PCA, Skokie, IL, 1997).

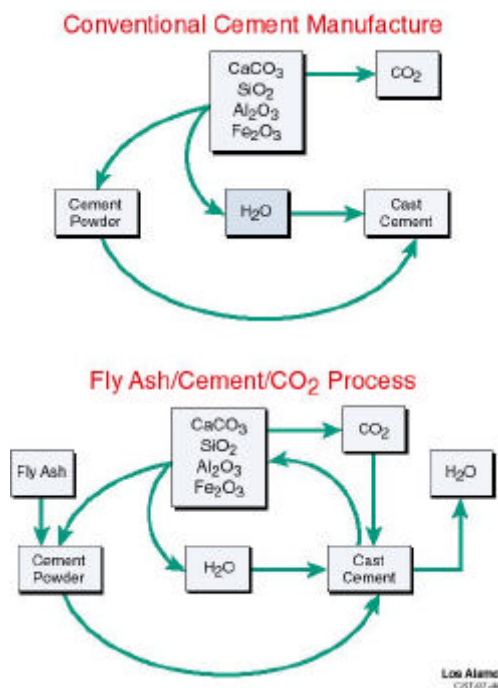


Figure 11. Process flow diagram for the manufacture of unmodified (conventional) and fly ash modified portland cement using supercritical CO<sub>2</sub>.